Supporting Information

Synthesis and aggregate formation of triphenylene core-centered porphyrin hexamers

Taku Hasobe,* Mohammad Gulam Rabbani, Atula S. D. Sandanayaka, Hayato Sakai and Tatsuya Murakami

Experimental Section

General Information. TPOAc was purchased from Tokyo Chemical Industry (TCI). All solvents and reagents of the best grade available were purchased from commercial suppliers and were used without further purification. All experiments were performed at room temperature. FTIR measurement was performed on a KBr plate by JASCO FT/IR-5300. ^{1}H NMR spectra were acquired on a 300 MHz Varian spectrometer, using the solvent peak as the reference standard, with chemical shifts given in parts per million. $CDCl_3$ and toluene-d_8 were used as NMR solvents.

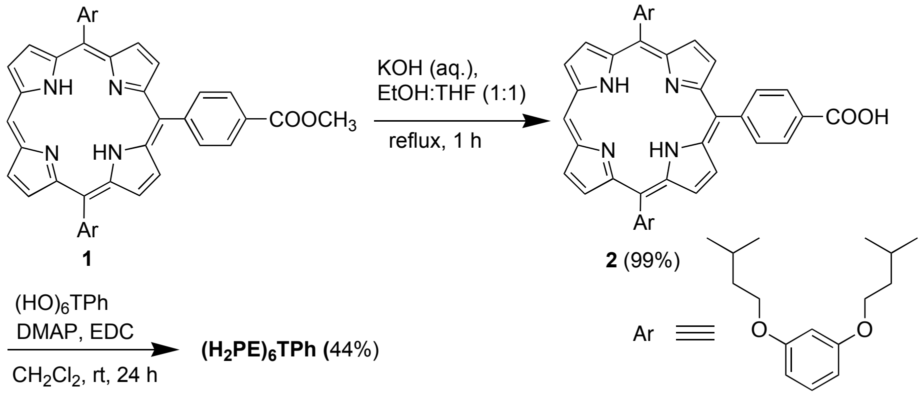
TEM Measurement. Transmission electron micrograph (TEM) measurements were recorded by applying a drop of the sample to a copper grid. Images were recorded on a Hitachi H 7100 transmission electron microscope an accelerating voltage of 100 kV for imaging.

AFM Measurement. Sample surface morphologies were analyzed with atomic force microscopy (AFM) using a Nanoscope III (Veeco Instruments), fitted with a 20 μm scan. Scanning was performed in tapping mode. The AFM was operated at scan rate = 1 Hz.

Steady-State Spectroscopic Measurements. Steady-state absorption spectra in the visible and near-IR regions were measured on a Perkin Elmer (Lamda 750) UV-VIS-NIR spectrophotometer. Fluorescence and excitation spectra were measured on a Perkin Elmer (LS-55) spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity.

X-Ray Diffraction Measurement. X-ray diffraction (XRD) measurement was carried out with a BRUKER-axs M18XHF-SRA using filtered Cu Kα radiation. The sample for XRD analysis was prepared by drying solution over a substrate in air.

Measurement of Photoelectrochemical Solar Dells. Photoelectrochemical measurements were carried out in a standard two-compartment cell consisting of a working electrode and a Pt wire gauze counter electrode in the electrolyte. The electrolyte is 0.5 M LiI and 0.01 M I_2 in acetonitrile. KEITHLEY 2400 was used for recording photocurrent and photovoltage responses under AM1.5 simulated light source (OTENTO-SUN II, Bunkoh-Keiki Co.,LTD). In the case of IPCE measurement, a monochromator (SM-25, Bunkoh-Keiki Co.,LTD) was introduced into the path of the excitation beam (300 W Xenon lamp, Bunkoh-Keiki Co.,LTD) for the selected wavelength. The lamp intensity at each wavelength was determined by Si photodiode (Hamamatsu Photonics S1337-1010BQ) and corrected.



Scheme S1. Synthetic details of $(H_2PE)_6TPh$ in this study.

Synthesis

5,15-bis(3,5-di-isoamyloxyphenyl)-10-(4-carboxylphenyl)porphyrin **2.** 5,15-bis(3,5-di-isoamyloxyphenyl)-10-(4-methoxycarbonylphenyl)porphyrin (**H_2PE**) was synthesized according to published procedure.[1] A mixture of **H_2PE** (1.14 g, 1.21 mmol) in 700 mL of THF-ethanol (1:1) and 70 mL of 2M KOH aqueous solution was refluxed (80 ºC) under an atmospheric pressure of nitrogen for 1 h. After cooling, the solvents were evaporated to dryness and then added 300 mL of water and 300 mL of $CHCl_3$. After neutralization (pH 7) with dilute HCl aqueous solution, organic phase was extracted, washed with water and dried over Na_2SO_4. After evaporation, the residue was washed with MeOH and dried under vacuum to give **2** as a dark reddish purple solid (1.10 g, 1.19 mmol, 99%). mp 284 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.22 (s, 1H), 9.33 (d, *J* = 6.4 Hz, 2H), 9.15 (d, *J* = 6.4 Hz, 2H), 9.06 (d, *J* = 6.8 Hz, 2H), 8.84 (d, *J* = 6.4 Hz, 2H), 8.56 (d, *J* = 10.8 Hz, 2H), 8.36 (d, *J* = 10.4 Hz, 2H), 7.41 (d, *J* = 2.8 Hz, 4H), 6.91 (t, *J* = 3.2 Hz, 2H), 4.17 (t, *J* = 8.8 Hz, 8H), 1.89 (m, 4H), 1.78 (q, *J* = 8.8 Hz, 8H), 0.99 (d, *J* = 8.8 Hz, 24H), -3.02 (s, 2H); MALDI-TOF-MS 927 ($M+H^+$).

$(H_2PE)_6$TPh. A mixture of porphyrin monomer **2** (1.10 g, 1.19 mmol), 2,3,6,7,10,11-hexahydroxytriphenylene ($(HO)_6$TPh, 49.0 mg, 0.15 mmol), DMAP (1.32 g, 10.8 mmol), EDC (2.07 g, 10.8 mmol) in 80 mL of dry CH_2Cl_2 was stirred at room temperature for 24 h under nitrogen atmosphere. The reaction mixture was quenched with water and the product was extracted with $CHCl_3$, washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulting product was isolated by flash column chromatography on silica gel ($CHCl_3$) and final purification was performed by gel permeation chromatography (BIO-RAD Bio-Beads® SX-1 Beads (200-400 Mesh), toluene) to afford hexakis porphyrin 1 as a dark reddish purple solid (370 mg, 0.064 mmol, 44%). mp 235 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.18 (s, 6H), 9.28 (d, *J* = 6.4 Hz, 12H), 9.05 (d, *J* = 6.4 Hz, 12H), 8.88 (m, 36H), 8.49 (d, *J* = 10.8 Hz, 12H), 7.22 (d, *J* = 3.2 Hz, 24H), 6.60 (t, *J* = 2.8 Hz, 12H), 3.86 (t, *J* = 8.8 Hz, 48H), 1.63 (m, 24H), 1.47 (q, *J* = 8.8 Hz, 48H), 0.73 (d, *J* = 8.8 Hz, 144H), -3.09 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 164.74, 158.21, 148.71, 146.74, 143.07, 135.12, 131.56, 131.24, 130.80, 128.75, 128.46, 128.39, 119.78, 118.91, 118.45, 114.39, 105.08, 100.78, 66.43, 37.83, 24.86, 22.42; MALDI-TOF-MS 5780 ($M+H^+$); UV-vis (THF, λ/nm, log(ε/dm^3 mol^{-1} cm^{-1})) 414 (6.38). Anal. cald for $C_{372}H_{396}N_{24}O_{36}$: C, 77.31; H, 6.91; N, 5.82. Found: C, 77.12; H, 7.08; N, 5.79.

H_2PA. 4-Acetamidophenyldipyrromethane (6.01 g, 21.5 mmol), dipyrromethane (2.12 g, 14.3 mmol), and

3,5-di-isoamyloxybenzaldehyde (10.11 g, 35.8 mmol) were dissolved in 2.15 L of dry $CHCl_3$. Trifluoroacetic acid (3.6 mL) was added, and the mixture was stirred for 3 h in the dark. *p*-Chloranil was added, and the mixture was stirred for additional 14 h. The reaction mixture was quenched by addition of 64 mL of triethylamine and the solvent was evaporated. Flash column chromatography on silica gel with $CHCl_3$/ethyl acetate (30:1 v/v) as the eluent afforded compound **H_2PA** as a dark reddish brown solid (830 mg, 0.88 mmol, 6.2%). mp 128 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.19 (s, 1H), 9.31 (d, *J* = 6.0 Hz, 2H), 9.12 (d, *J* = 6.0 Hz, 2H), 9.01 (d, *J* = 6.4 Hz, 2H), 8.86 (d, *J* = 6.4 Hz, 2H), 8.14 (d, *J* = 11.2 Hz, 2H), 7.86 (d, *J* = 11.2 Hz, 2H), 7.48 (br s, 1H), 7.39 (d, *J* = 2.8 Hz, 4H), 6.90 (t, *J* = 2.8 Hz, 2H), 4.16 (t, *J* = 8.8 Hz, 8H), 2.35 (s, 3H), 1.87 (m, 4H), 1.78 (q, *J* = 8.8 Hz, 8H), 0.98 (d, *J* = 8.4 Hz, 24H), -3.04 (br. s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 168.47, 158.43, 143.48, 138.53, 137.57, 134.99, 131.51, 131.24, 130.79, 119.75, 119.55, 117.83, 114.47, 104.72, 101.01, 66.76, 38.14, 25.13, 24.87, 22.66; MALDI-TOF-MS 941 (M + H^+); UV-vis (THF, λ/nm, log(ε/dm^3 mol^{-1} cm^{-1})) 414 (5.62). Anal. cald for $C_{60}H_{69}N_5O_5$: C, 76.65; H, 7.40; N, 7.45. Found: C, 76.36; H, 7.41; N, 7.37.

3. **H_2PA** (820 mg, 0.87 mmol) was dissolved in a mixture of EtOH (260 mL) and concd HCl solution (175 mL) and refluxed at 80 ºC for 17 h. After cooling, the reaction mixture was poured onto water, and the organic layer was extracted with $CHCl_3$, washed with aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and evaporated. Flash column chromatography on silica gel with $CHCl_3$ as the eluent afforded compound **3** as a dark reddish brown solid (697 mg, 0.78 mmol, 89%). Mp 124 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.15 (s, 1H), 9.30 (d, *J* = 6.4 Hz, 2H), 9.11 (d, *J* = 6.0 Hz, 2H), 9.00 (d, *J* = 6.4 Hz, 2H), 8.94 (d, *J* = 6.8 Hz, 2H), 7.97 (d, *J* = 11.2 Hz, 2H), 7.39 (d, *J* = 3.2 Hz, 4H), 7.05 (d, *J* = 11.2 Hz, 2H), 6.89 (t, *J* = 3.2 Hz, 2H), 4.16 (t, *J* = 8.8 Hz, 8H), 4.02 (br s, 2H), 1.90 (m, 4H), 1.77 (q, *J* = 8.8 Hz, 8H), 0.98 (d, *J* = 8.8 Hz, 24H), -3.02 (br. s, 2H); MALDI-TOF-MS 899 (M + H^+).

4. A solution of THF containing 4-dimethylaminopyridine (DMAP, 408 mg, 3.34 mmol), 1-hydroxybenzotriazole (HOBt, 450 mg, 3.34 mmol) and 6-bromohexanoic acid (651 mg, 3.34 mmol) was treated with 1-ethyl-3-(3-dimehylaminopropyl)-carbodiimide hydrochloride (EDC, 640 mg, 3.34 mmol) under nitrogen at 0 ºC. The mixture was stirred at 0 ºC for 1h. Compound **3** (300 mg, 0.334 mmol) was added to the mixture and stirred at 0 ºC for 30 min. The mixture was then stirred at room temperature overnight. The mixture was concentrated in vacuo and poured onto a 2% HCl aqueous solution and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aqueous solution, dried over anhydrous Na_2SO_4 and evaporated the solvent. Flash column chromatography on silica gel with $CHCl_3$ as the eluent afforded compound **4** as a dark reddish brown solid (327 mg, 0.30 mmol, 91%). mp 112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.19 (s, 1H), 9.31 (d, *J* = 6.0 Hz, 2H), 9.12 (d, *J* = 6.0 Hz, 2H), 9.01 (d, *J* = 6.4 Hz, 2H), 8.86 (d, *J* = 6.4 Hz, 2H), 8.15 (d, *J* = 11.2 Hz, 2H), 7.89 (d, *J* = 11.2 Hz, 2H), 7.45 (br s, 1H), 7.39 (d, *J* = 2.8 Hz, 4H), 6.89 (t, *J* = 2.8 Hz, 2H), 4.16 (t, *J* = 8.8 Hz, 8H), 3.50 (t, *J* = 8.8 Hz, 2H), 2.55 (t, *J* = 10.0 Hz, 2H), 1.99 (m, 2H), 1.87 (m, 6H), 1. (q, *J* = 8.8 Hz, 8H), 0.97 (d, *J* = 8.8 Hz, 24H), -3.04 (br. s, 2H); MALDI-TOF-MS 1075 (M + H^+).

5. A solution of THF containing 4-dimethylaminopyridine (DMAP, 340 mg, 2.78 mmol), 1-hydroxybenzotriazole (HOBt, 375 mg, 2.78 mmol) and 6-bromohexadecanoic acid (932 mg, 2.78 mmol) was treated with 1-ethyl-3-(3-dimehylaminopropyl)-carbodiimide hydrochloride (EDC, 533 mg, 2.78 mmol) under nitrogen at 0 °C. The mixture was stirred at 0 °C for 1h. Compound **3** (250 mg, 0.278 mmol) was added to the mixture and stirred at 0 °C for 30 min. The mixture was then stirred at room temperature overnight. The mixture was concentrated in vacuo and poured onto a 2% HCl aqueous solution and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aqueous solution, dried over anhydrous Na_2SO_4 and evaporated the solvent. Flash column chromatography on silica gel with $CHCl_3$ as the eluent afforded compound **5** as a dark reddish brown solid (244 mg, 0.20 mmol, 72%). mp 73 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.19 (s, 1H), 9.31 (d, *J* = 6.0 Hz, 2H), 9.12 (d, *J* = 6.4 Hz, 2H), 9.01 (d, *J* = 6.4 Hz, 2H), 8.87 (d, *J* = 6.0 Hz, 2H), 8.14 (d, *J* = 11.6 Hz, 2H), 7.88 (d, *J* = 11.2 Hz, 2H), 7.44 (br s, 1H), 7.39 (d, *J* = 3.2 Hz, 4H), 6.90 (t, *J* = 2.8 Hz, 2H), 4.16 (t, *J* = 9.2 Hz, 8H), 3.39 (t, *J* = 9.2 Hz, 2H), 2.52 (t, *J* = 9.6 Hz, 2H), 1.93-1.74 (m, 16 H), 1.53-1.29 (m, 24H), 0.98 (d, *J* = 8.8 Hz, 24H), -3.04 (br. s, 2H); MALDI-TOF-MS 1216 (M + H^+).

$(H_2PAC_5)_6$TPh. To a solution of porphyrin **4** (320 mg, 0.298 mmol) in dry DMF (8 mL) was added $(HO)_6$TPh (15.32 mg, 0.047 mmol) and K_2CO_3 (200 mg) The mixture was stirred overnight at 75 °C under nitrogen atmosphere. The reaction mixture was poured into water and extracted with CH_2Cl_2, washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulting product was isolated by flash column chromatography on silica gel (CH_2Cl_2) and final purification was performed by gel permeation chromatography (BIO-RAD Bio-Beads® SX-1 Beads (200-400 Mesh), toluene) to afford **$(H_2PAC_5)_6$TPh** as a dark reddish purple solid (235 mg, 0.037 mmol, 77%). mp 173 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.14 (s, 6H), 9.27 (d, *J* = 6.0 Hz, 12H), 9.08 (d, *J* = 6.0 Hz, 12H), 8.94 (d, *J* = 6.4 Hz, 12H), 8.81 (d, *J* = 6.8 Hz, 12H), 8.06 (d, *J* = 10.8 Hz, 12H), 7.94 (br s, 12H), 7.80 (d, *J* = 11.2 Hz, 12H), 7.34 (d, *J* = 2.8 Hz, 24H), 6.83 (t, *J* = 2.8 Hz, 12H), 4.25 (t, *J* = 8.0 Hz, 12H) 4.07 (t, *J* = 8.8 Hz, 48H), 2.36 (t, J = 8.0 Hz, 12H), 1.94-1.63 (m, 108 H), 0.88 (d, J = 8.4 Hz, 144H), -3.07 (br. s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 171.92, 158.37, 148.96, 143.39, 138.31, 137.76, 134.89, 131.46, 131.20, 131.08, 130.77, 123.75, 119.82, 119.52, 117.92, 114.42, 107.43, 104.64, 100.95, 69.39, 66.67, 38.04, 29.13, 26.10, 25.45, 25.04, 22.59; MALDI-TOF-MS 6290 ($M+H^+$); UV-vis (THF, λ/nm, log(ε/dm^3 mol^{-1} cm^{-1})) 414 (6.39). Anal. cald for $C_{402}H_{462}N_{30}O_{36}$: C, 76.76; H, 7.40; N, 6.68. Found: C, 76.54; H, 4.51; N, 6.49.

$(H_2PAC_{15})_6$TPh. To a solution of porphyrin **5** (240 mg, 0.197 mmol) in dry DMF (8 mL) was added $(HO)_6$TPh (9.75 mg, 0.030 mmol) and K_2CO_3 (135 mg) The mixture was stirred overnight at 75 ºC under nitrogen atmosphere. The reaction mixture was poured into water and extracted with CH_2Cl_2, washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulting product was isolated by flash column chromatography on silica gel (CH_2Cl_2) and final purification was performed by gel permeation chromatography (BIO-RAD Bio-Beads® SX-1 Beads (200-400 Mesh), toluene) to afford **$(H_2PAC_{15})_6$TPh** as a dark reddish purple solid (165 mg, 0.023 mmol, 77%). mp 144 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.15 (s, 6H), 9.28 (d, J = 6.0 Hz, 12H), 9.11 (d, J = 6.4 Hz, 12H), 9.00 (d, J = 6.0 Hz, 12H), 8.85 (d, J = 6.4 Hz, 12H), 8.10 (d, J = 10.8 Hz, 12H), 7.85 (s, 6H), 7.80 (d, J = 10.8 Hz, 12H), 7.50 (br s, 6H), 7.38 (d, J = 3.2 Hz, 24H), 6.89 (t, J = 2.8 Hz, 12H), 4.24 (t, J = 8.4 Hz, 12H), 4.13 (t, J = 8.8 Hz, 48H), 2.37 (t, J = 10.4 Hz, 12H), 1.95-1.70 (m, 96H), 1.58 (t, J = 8.0 Hz, 12H), 1.60-1.27 (m, 120H), 0.95 (d, J = 8.8 Hz, 144H), -3.04 (br. s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 171.77, 158.42, 148.96, 143.46, 138.29, 137.69, 134.93, 131.49, 131.29, 131.12, 130.78, 123.61, 119.84, 119.52, 117.78, 114.45, 107.33, 104.69, 100.99, 69.74, 66.73, 38.11, 37.93, 29.74, 29.72, 29.61, 29.54, 29.51, 29.42, 26.23, 25.74, 25.10; MALDI-TOF-MS 7132 ($M+H^+$); UV-vis (THF, λ/nm, log(ε/dm^3 mol^{-1} cm^{-1})) 414 (6.41). Anal. cald for $C_{462}H_{582}N_{30}O_{36}$: C, 77.81; H, 8.23; N, 5.89. Found: C, 77.52; H, 8.19; N, 5.89.

$TPOC_{16}H_{33}$. **$TPOC_{16}H_{33}$** was synthesized according to a reported method with a slight modification.[2] To a solution of **$(HO)_6$TPh** (209 mg, 0.64 mmol) in dry DMF (8 mL) was added 1-bromohexadecane (2.36 mL, 2.36 mmol) and K_2CO_3 (1.1 g). The mixture was stirred for 24 h at 80 ºC under nitrogen atmosphere. After cool down, the reaction mixture was poured into water and extracted with $CHCl_3$, washed with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulting product was isolated by flash column chromatography on silica gel with $CHCl_3$/hexane (1:1) as eluent. Final purification performed by recrystallization from EtOH afforded **$TPOC_{16}H_{33}$** as a white solid (788 mg, 0.47 mmol, 74%). mp 63 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.83 (s, 6H), 4.22 (d, *J* = 8.8 Hz, 12H), 1.98-1.89 (m, 12H), 1.62-1.52 (m, 12H), 1.46-1.19 (m, 144H), 0.88 (t, *J* = 8.8 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 148.97, 123.61, 107.39, 69.74, 31.94, 29.74, 29.70, 29.68, 29.56, 29.50, 29.38, 26.23, 22.71, 14.12; MALDI-TOF-MS 1671 ($M+H^+$); UV-vis ($CHCl_3$, λ/nm, log(ε/dm^3 mol^{-1} cm^{-1})) 278 (5.09). Anal. cald for $C_{114}H_{204}O_6$: C, 81.95; H, 12.31. Found: C, 81.71; H, 12.35.

References

1. T. Hasobe, H. Imahori, K. Ohkubo, H. Yamada, T. Sato, Y. Nishimura, I. Yamazaki and S. Fukuzumi, *J. Porphyrins Phthalocyanines*, 2003, **7**, 296.
2. E. Voisin and V. E. Williams, *Macromolecules*, 2008, **41**, 2994.

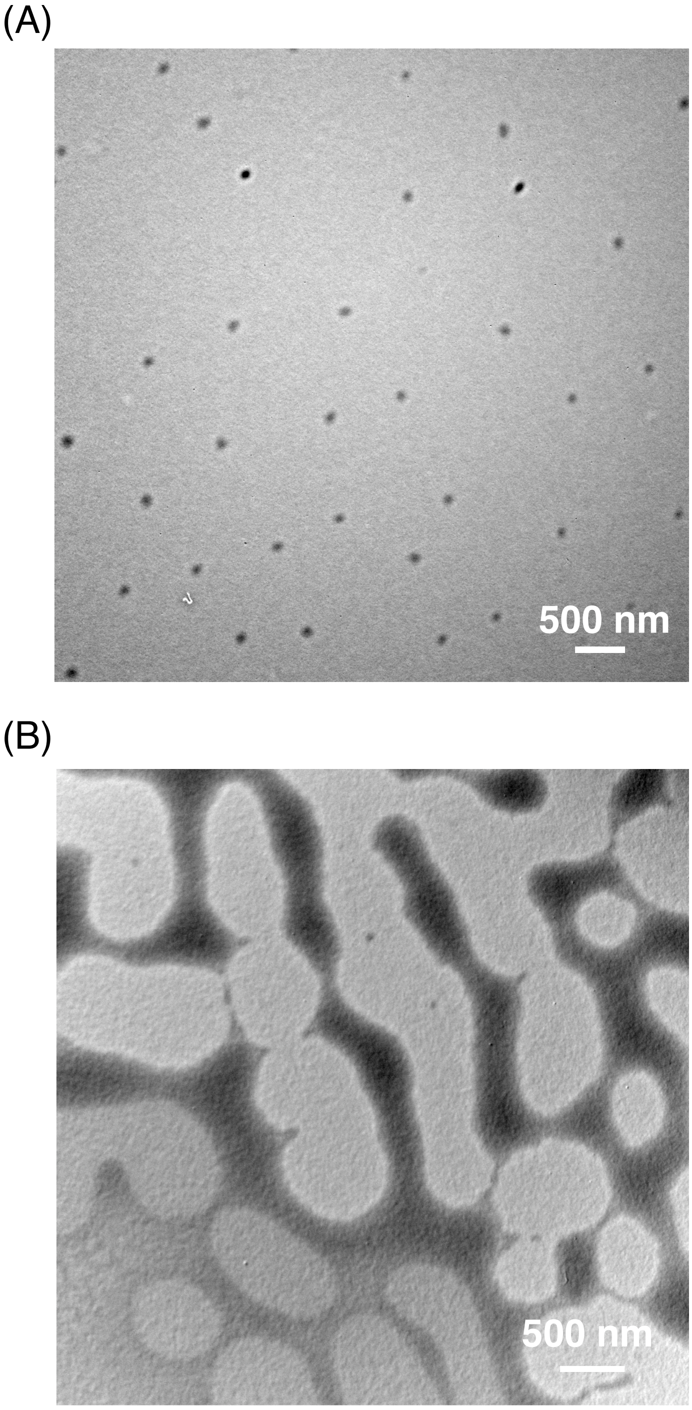


Fig. S1 TEM images of (H_2PAC_{15})$_6$TPh patterns prepared in toluene solution. The original concentration: (A) 2 μM and (B) 100 μM.

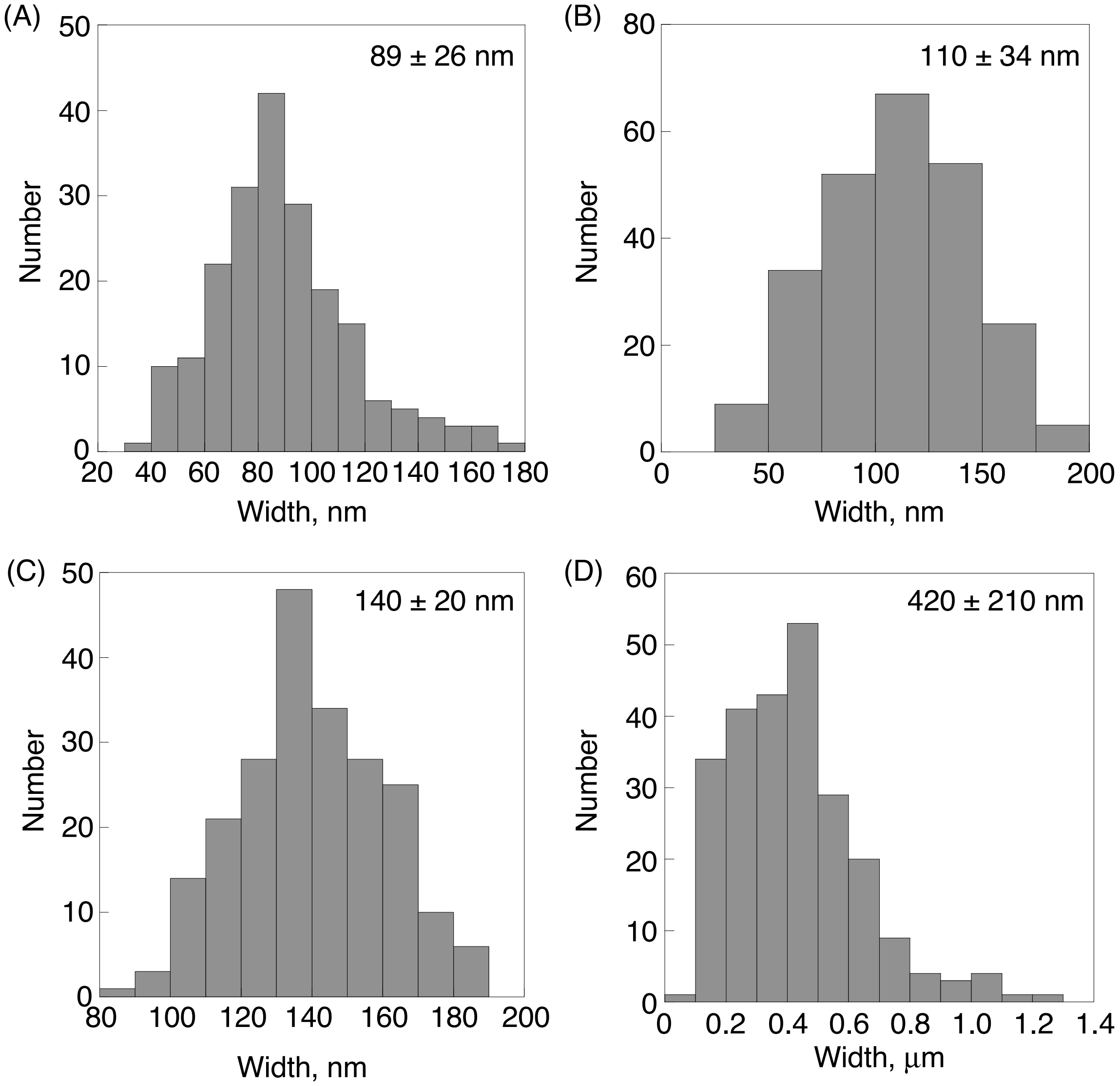


Fig. S2 Width distributions of (A) $(H_2PE)_6TPh$ pattern, (B) $(H_2PAC_5)_6TPh$ pattern, (C) $(H_2PAC_{15})_6TPh$ pattern and (D) $TPOC_{16}H_{33}$ fiber.

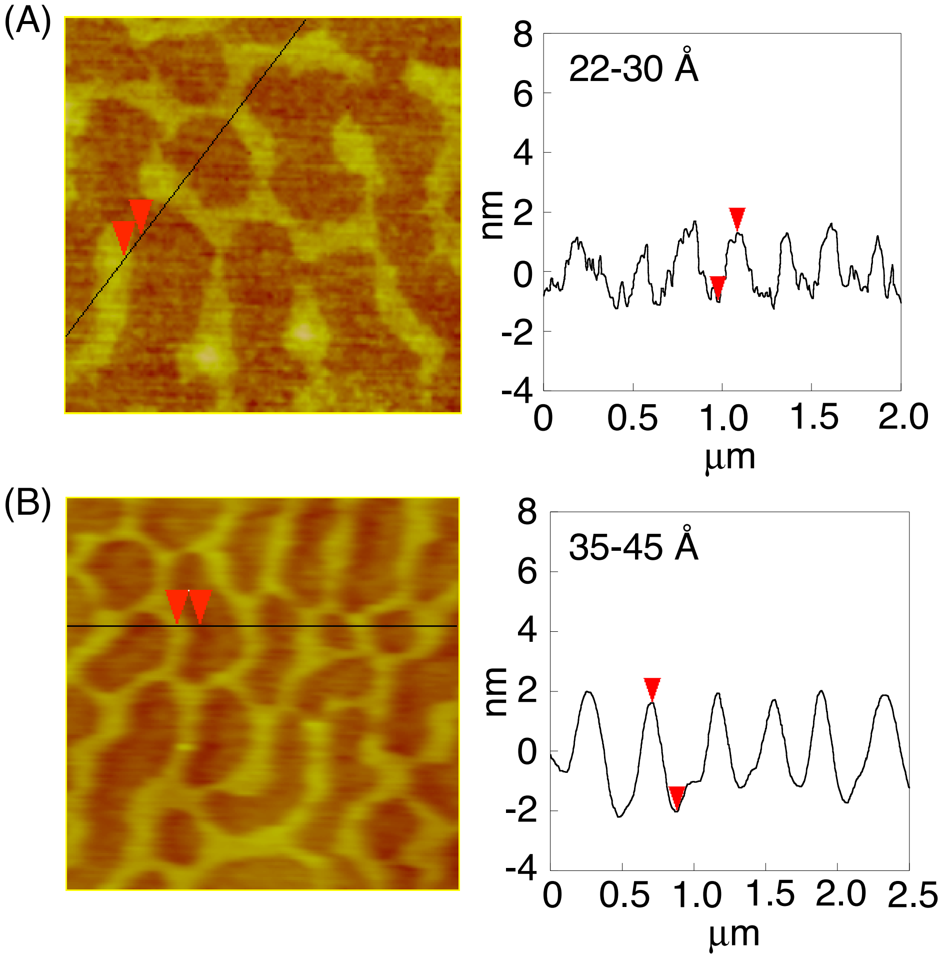
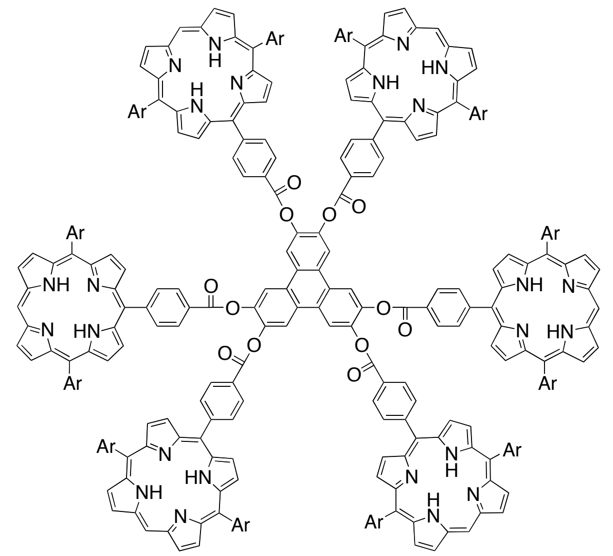


Fig. S3 AFM images of (A) $(H_2PE)_6TPh$ patterns and (B) $(H_2PAC_5)_6TPh$ patterns on the carbon-coated copper film (TEM grid).



(H$_2$PE)$_6$TPh

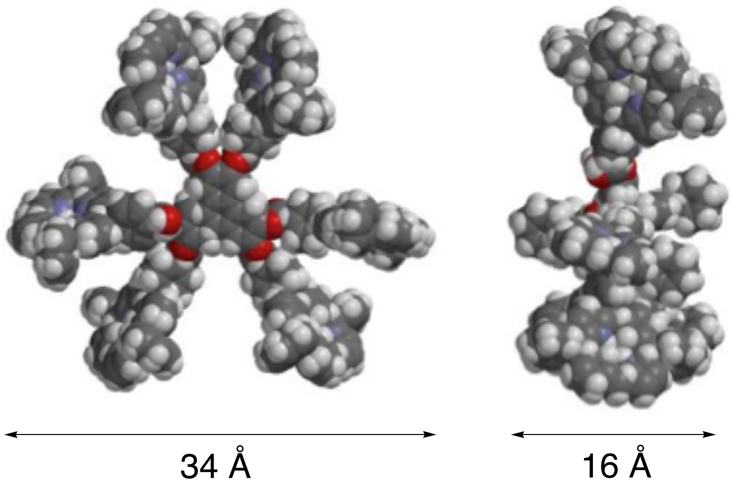
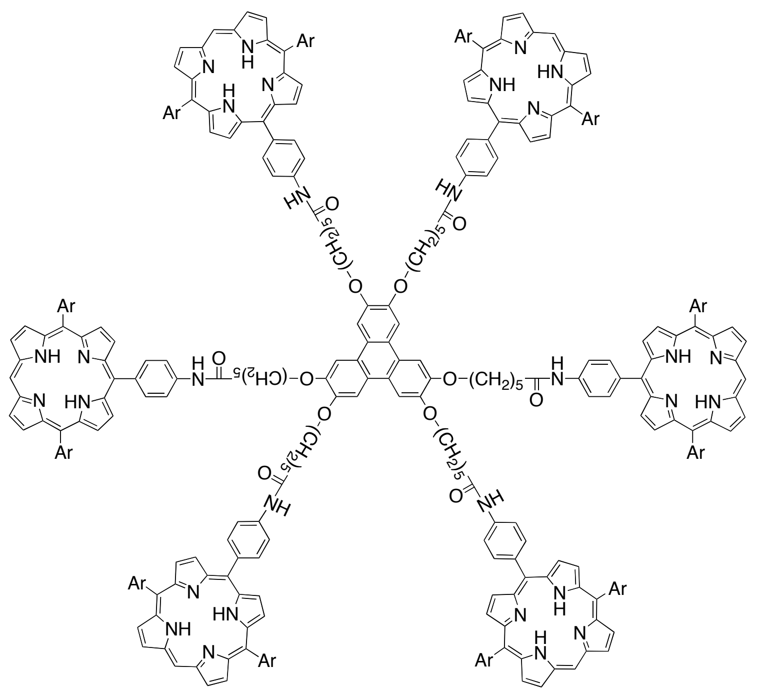


Fig. S4 Optimized structure of **(H$_2$PE)$_6$TPh** obtained by DFT calculation (B3LYP/3-21G* basis set). 3,5-di-isoamyloxyl phenyl groups are omitted.



$(H_2PAC_5)_6TPh$ (n = 5)

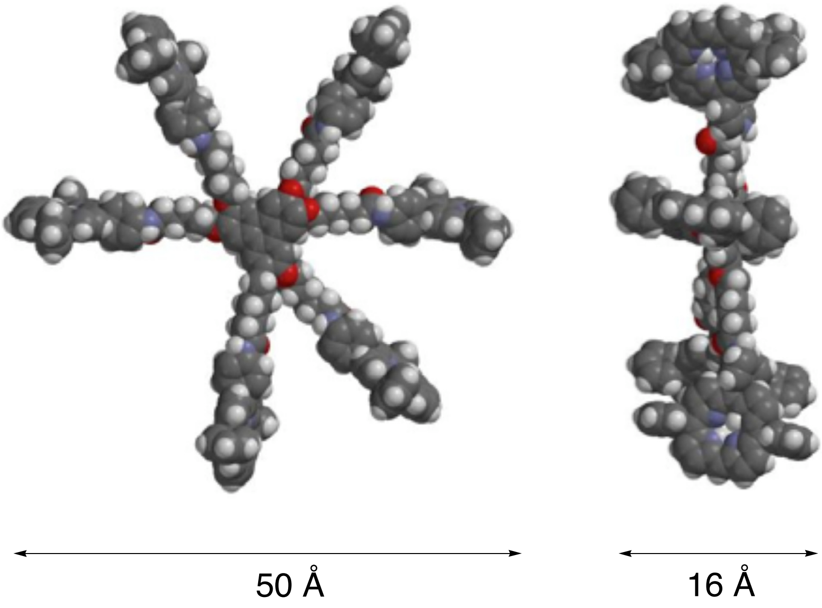
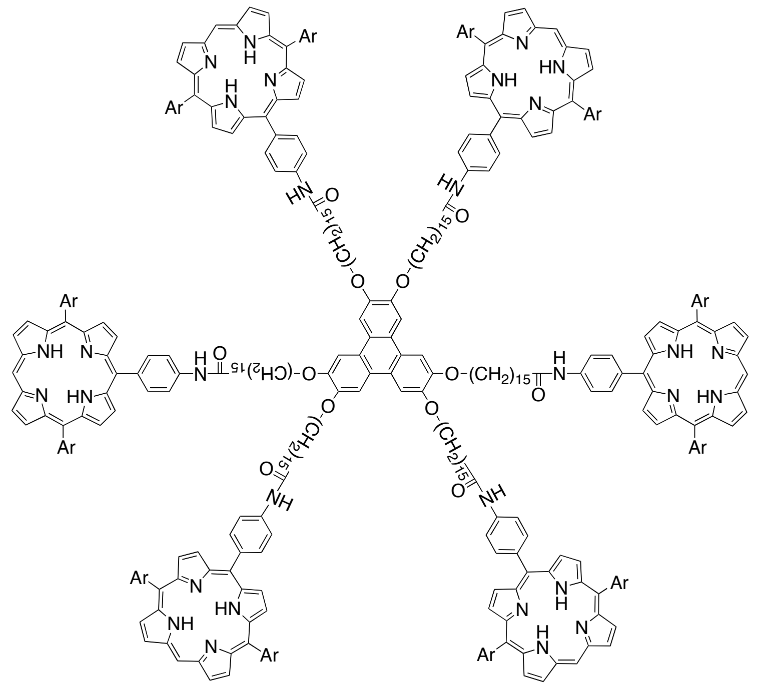


Fig. S5 Optimized structure of **$(H_2PAC_5)_6TPh$** obtained by DFT calculation (B3LYP/3-21G* basis set). 3,5-di-isoamyloxyl phenyl groups are omitted.



$(H_2PAC_{15})_6TPh$ (n = 15)

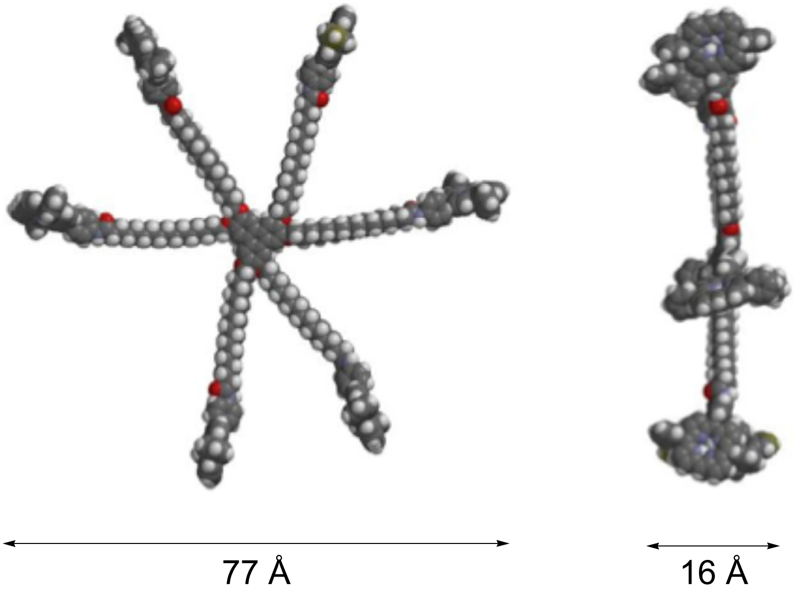


Fig. S6 Optimized structure of **$(H_2PAC_{15})_6TPh$** obtained by DFT calculation (B3LYP/3-21G* basis set). 3,5-di-isoamyloxyl phenyl groups are omitted.

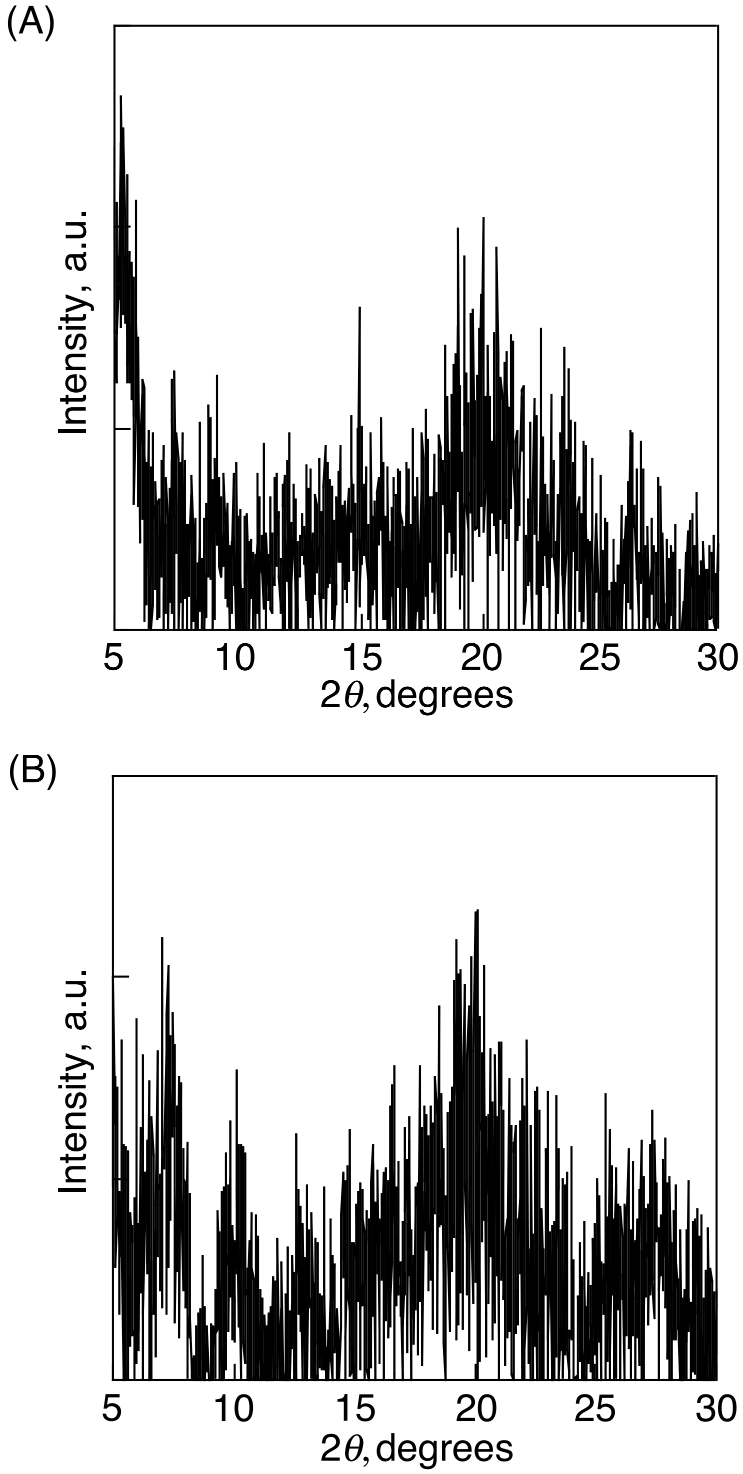


Fig. S7 XRD data of (A) $(H_2PAC_{15})_6$TPh starting materials and (B) $(H_2PE)_6$TPh patterns.

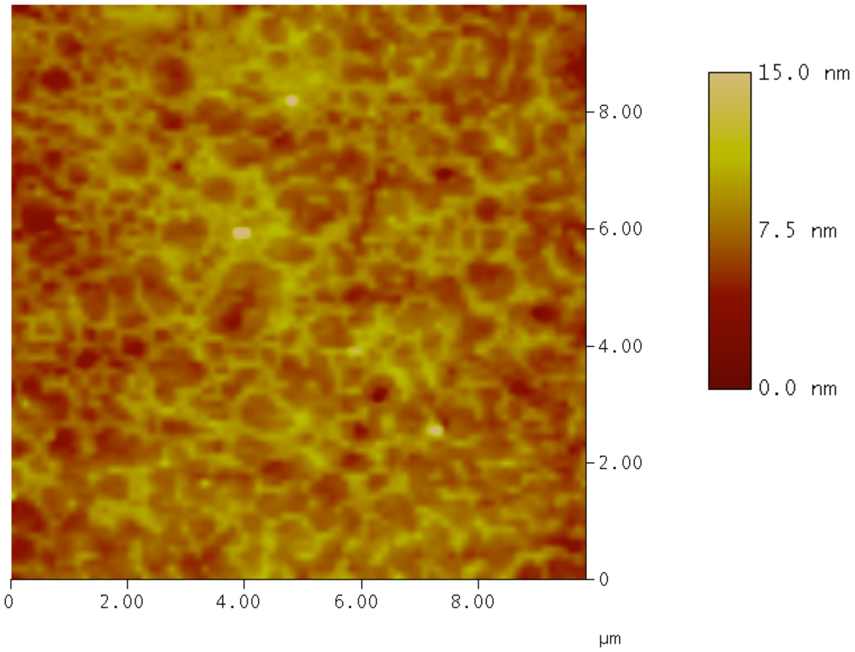


Fig. S8 AFM images of $(H_2PAC_{15})_6$TPh patterns on a quartz plate.

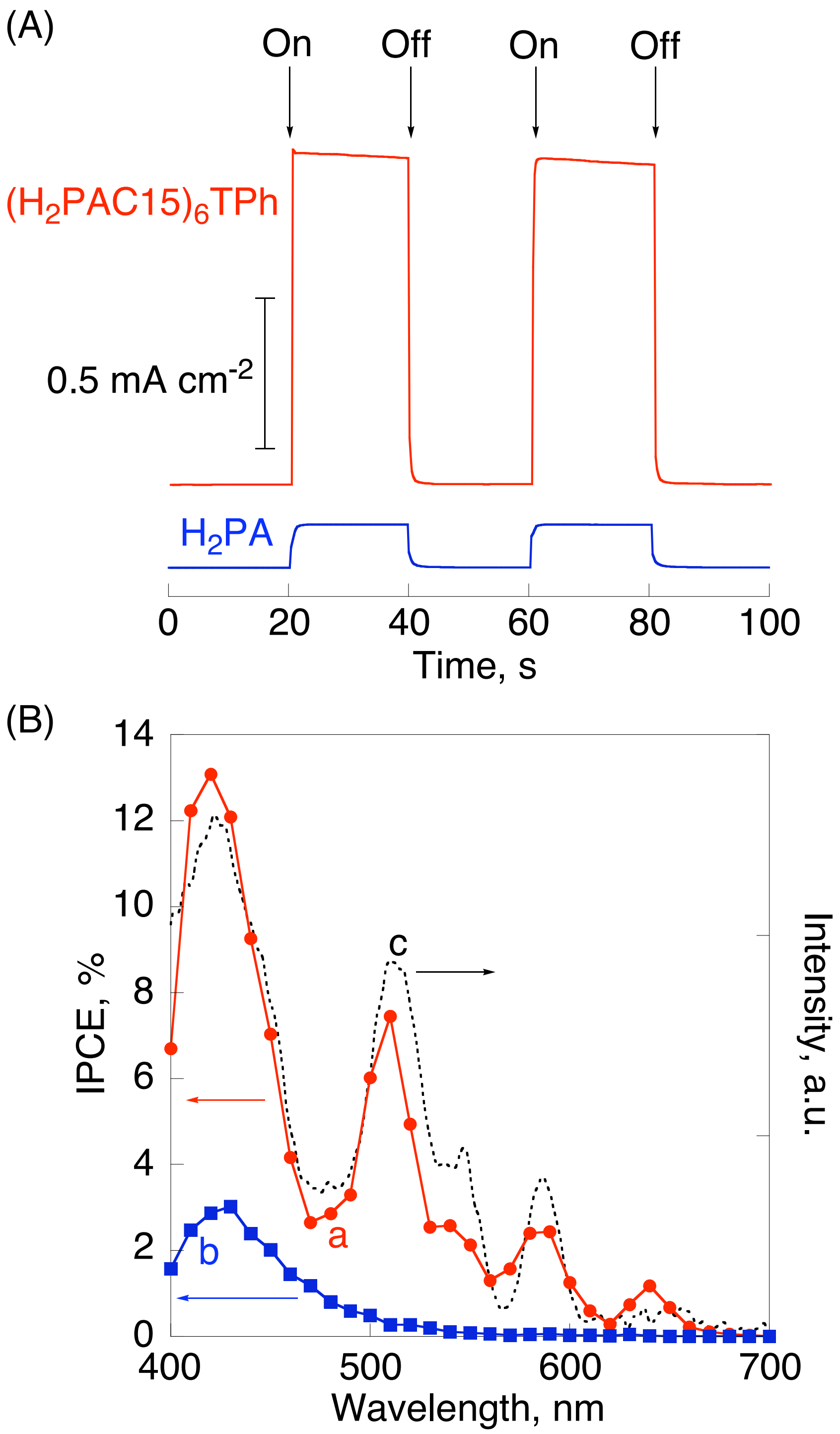


Fig. S9 (A) Photocurrent responses of $(H_2PAC_{15})_6TPh$ pattern and H_2PA reference assembly on Optically transparent electrodes (OTE) under white light illumination (AM 1.5 condition: 100 mW cm^{-2}). (B) Photocurrent action spectra of (a) $(H_2PAC_{15})_6TPh$ pattern and (b) H_2PA assembly on OTE films. (c) Excitation spectrum of $(H_2PAC_{15})_6TPh$ pattern on OTE. The incident photon to current conversion efficiency (IPCE) values were calculated by the following: IPCE (%) = $100 \times 1240 \times I_{sc} / (I_{inc} \times \lambda)$, where I_{sc} is the short circuit photocurrent (A/cm^2), I_{inc} is the incident light intensity (W/cm^2), and λ is the wavelength (nm).

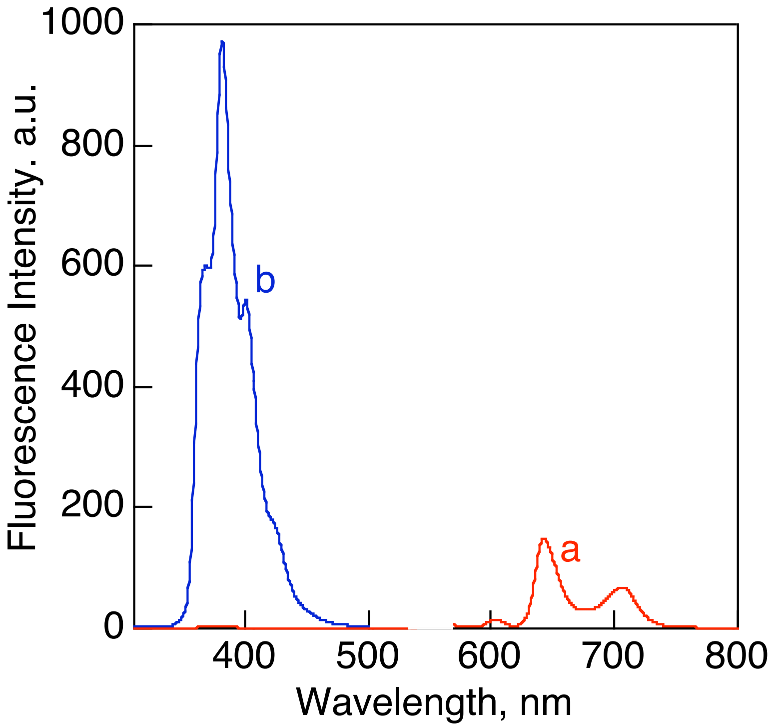


Fig. S10 Fluorescence spectra of (a) 0.25 μM $(H_2PAC_{15})_6TPh$ and (b) 0.25 μM $TPOC_{16}H_{33}$ in THF. Excitation wavelength is 279 nm.

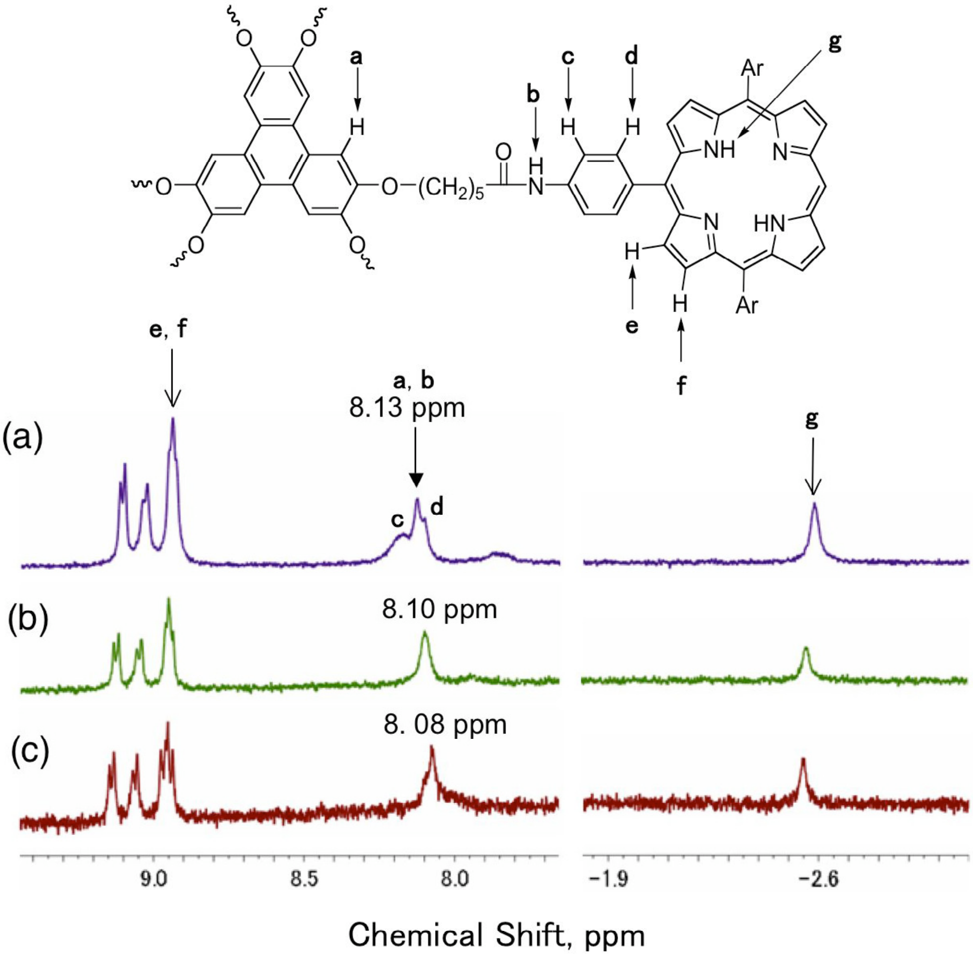


Fig. S11 NMR spectra of $(H_2PAC_5)_6$TPh of the aromatic and pyrrole NH proton regions in toluene-d_8 as a function of concentration. (a) 1.0 mM, (b) 0.25 mM and (c) 0.12 mM.

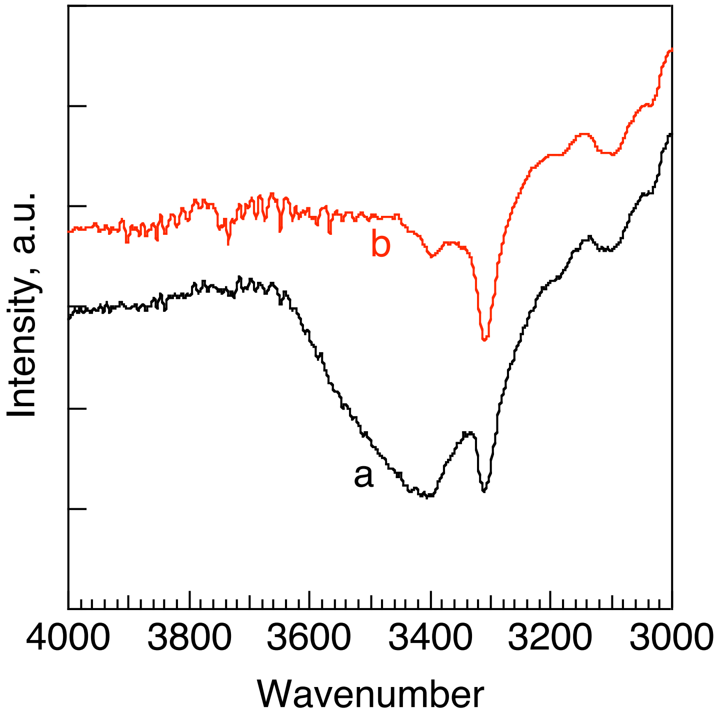


Fig. S12 FTIR spectra of (a) $(H_2PAC_{15})_6$TPh pattern and (b) $(H_2PAC_{15})_6$TPh (powder).